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THE BROMIDE CONTENT IN THE HALOGENIDES OF FOOD AND OF BODY FLUIDS

M. R. Bloch, D. Kaplan and J. Schnerb
Dead Sea Works Ltd., Beer Sheba

ABSTRACT

The correlation of the ratio Cl^-/Br^- in food with that in body fluids is discussed on the basis of the determination of the ratio Cl^-/Br^- in water, vegetables, fruit, animal products, salt and body fluids. It seems that a regulating mechanism of the kidney counterbalances changes of common salt content in the diet by retaining bromide in preference to chloride.

The chloride ions contained in human and animal diets are always accompanied by bromide ions. Variations in the ratio of chloride to bromide ions in food and body fluids and excretions have been investigated. A method has been developed for determining bromide ions without destroying organic matter.

A. BROMIDE ION DETERMINATION IN PLANT AND ANIMAL TISSUE

In a recent publication (Kaplan and Schnerb 1958) a semimicroanalytical method was reported for the determination of Br^- in fluids containing only a small amount (about 1 mg %) of bromide; examples were given of the determination of bromide in physiological fluids such as urine, blood serum, sweat and saliva. According to this method, the halogenides are precipitated with silver nitrate (in case the chloride content is very low, sodium chloride is added before precipitation). The precipitated silver halogenides are then reduced with zinc. The bromide in the resulting zinc halogenide solution is determined according to a modified van der Meulen (1931) procedure (Bloch, Kertes and Schnerb 1952). About 1 ml of serum was required in order to determine the bromide content to within ± 3 % of its actual value.

The same method has now proved to be suitable for the determination of bromide in water, soils, food of both animal and vegetable origin, beverages, etc.

In the above publication, we pointed out that the methods described for bromide determination in living matter involved the initial destruction of the organic material, mostly by an alkaline ashing process, whilst according to our method, the bromide content could be analysed without a previous ashing treatment merely by extracting the material with water at room or higher temperatures.

Parallel determinations according to our method with and without ashing pretreatment showed no differences in the results.

Table I enables results obtained with and without ashing pretreatment respectively to be compared. The ashing process was carried out according to the generally accepted method of heating the material in the presence of soda ash to 500–550°C.

Received May 26, 1959

TABLE I

	After ashing		Without ashing	
	Cl^-(mg/100 g)	Br^-(mg/100 g)	Cl^-(mg/100 g)	Br^-(mg/100 g)
Wheat flour	73.57	1.945	73.2	1.97
Quaker oats	58.04	0.74	57.9	0.77
Apple	5.95	0.646	6.07	0.677
Banana	84.9	0.694	85.8	0.706
Avocado	23.3	0.67	23.3	0.65
Fish	96.9	0.833	97.6	0.82
Meat	61.2	1.50	62.0	1.47
White beer	22.66	0.265	22.66	0.23
Wine	6.6	0.295	6.3	0.267

In products containing proteins, starch, fats, etc., these must be removed. Proteins are removed by pretreatment with tungstic acid, starches are hydrolysed with mineral acid and fats are saponified with alkali. Typical examples of such pretreatment are given below:

1. *Meat, fish and eggs*

10 g of the material is leached with water at 65–70°C for 30 minutes, the protein is precipitated with 10 ml sodium tungstate (10%) and 10 ml 2/3 N H_2SO_4, the solution made up to the mark in a 50 ml or 100 ml volumetric flask and then filtered. The bromine is analysed on a 10 ml aliquot of the filtrate.

2. *Plants and flour*

10–15 g of the material (after crushing) is leached with hot water for 30 minutes; flour is leached with water at room temperature. In cases where the protein does not dissolve, e.g. oats, millets, etc., the solution is made up to the mark of a 100 ml volumetric flask, 45 ml aliquot is heated with 2 ml of 2N H_2SO_4 for 5 minutes, cooled, made up to the mark of a 50 ml volumetric fllask and bromide analysed on 10 ml of the resulting solution. If the protein of the plant is soluble, e.g. soya, the former is first removed with 15 ml sodium tungstate (10%) and 15 ml 2/3 N H_2SO_4

3. *Fruit*

20–50 g are crushed and leached with water at 65–70°C for 30 minutes. If the vegetables or fruit contain starch, e.g. tomatoes, avocados, pears, guavas, 2–4 ml of 2N H_2SO_4 (or 2N HCl) are added and the solution boiled for 2–5 minutes. After cooling, the solution is made up to the mark of a 100 ml volumetric flask and the bromide determined on a suitable aliquot.

4. *Beverages, such as wine and beer*

The CO_2 is removed by pouring from one glass to another, the colour is removed with activated carbon, 5 ml of NaOH (5%) is added to 40 ml of the filtrate, the solution made up to the mark of a 50 ml volumetric flask, and after a further filtration, the bromide is determined on 10 ml of the filtrate.

5. *Other materials*

Other materials, containing no or only a small amount of organic matter, like water or soils, need no special pretreatment. Soils, for instance, are leached with boiling water (50 g in 300 ml water during 10 minutes. The solution is then filtered into a 250 ml volumetric flask and after making up to the mark, 40 ml of the solution are concentrated to 10 ml and the bromide analysed after the addition of a small amount of sodium chloride.

Table II shows the results of a series of materials analysed according to the method described. Cl^- analysis in these materials and those mentioned in the following chapters was carried out with the mercurimetric method (Roberts 1936).

The results of the analyses of a variety of foodstuffs conform closely with those found by other authors (Beeson 1941, Damiens and Blaignon 1931–1932).

Most of the vegetables investigated have a relatively high bromide content and consequently a low Cl^-/Br^- ratio. Especially high figures for Br^- were found in apples, pears and some varieties of water melon. There seems to exist some regulating factor in the metabolism of bromide in certain plants which induces a preferred uptake of bromide from irrigation water. It is significant that cotton (50–54 in Table II) has an average Cl^-/Br^- ratio of 48 whereas the water with which it is irrigated has a ratio of 508 (55 in Table II).

TABLE II

No.	Name of material	Cl^- mg/100 g	Br^- mg/100 g	Cl^-/Br^-	Comments
1	Egg white	170,6	0.744	229.0	
	Egg yolk	191.0	0.925	206.0	
2	Egg white	198.6	0.540	368.0	
	Egg yolk	178.0	0.596	300.0	
3	Egg white	189.0	0.649	291.0	
	Egg yolk	190.0	0.840	226.0	
4	Egg white	185.5	0.525	353.0	
	Egg yolk	197.3	0.693	284.0	
5	Egg white	191.0	0.610	313.0	
	Egg yolk	181.0	0.504	359.0	
6	Milk	84.2	0.310	271.0	"Tnuva"
7	Fish	97.6	0.830	117.6	Carp
8	Fish	94.5	0.400	230.0	Frozen Norwegian sea-fish
9	Fish	90.0	0.500	180.0	Frozen Norwegian sea-fish
10	Meat	62.0	1.470	42.2	Calf
11	Blood from calf	367.0	1.600	230.0	
12	Melon	84.0	0.960	87.0	With peel
13	Melon	57.5	0.295	195.0	With peel
14	Melon	114.2	0.794	144.0	With peel
15	Water melon 1	5.85	0.082	71.3	Without peel

TABLE II

No.	Name of Material	Cl^- mg/100 g	Br^- mg/100 g	Cl^-/Br^-	Comments
16	Water melone 2	3.56	0.277	12.8	Without peel
17	Water melone 3	2.28	0.072	31.6	Without peel
18	Grapes	36.9	0.260	142.0	Green, unknown source
19	Grapes	5.46	0.106	51.5	Red, unknown source
20	Grapes	7.5	0.202	37.0	Green muskat "Kiryat Anavim"
21	Grapes	5.3	0.190	28.0	Red muskat "Kiryat Anavim"
22	Grapestone	19.9	0.63	31.6	
23	Apple	4.0	0.405	9.9	Mishmar Haemek
24	Apple	6.27	0.689	9.1	Neoth Mordechai
25	Pomegranate stone	41.7	0.624	66.8	Hasolelim, Sweet "Melici"
26	Pomegranate peel	230.0	2.370	97.0	
27	Guyava	79.0	0.825	95.7	
28	Pear	4.0	0.440	9.0	
29	Orange	5.93	0.300	19.8	Without peel "Washington"
30	Orange	12.12	0.266	45.5	
31	Orange Clementina	4.85	0.266	18.2	Without peel "Dansi"
32	Orange Clementina peel	12.9	1.530	8.4	
33	Grapefruit	9.8	0.335	29.2	Without peel
34	Peel of grapefruit	18.0	0.490	37.0	
35	Banana	106.7	1.410	76.0	14.12.57
36	Banana	85.5	0.706	121.0	5.1.58
37	Avucado	23.3	0.670	34.7	With peel
38	Potato	75.4	0.737	102.0	
39	Potato	129.8	1.034	125.0	
40	Tomato	72.6	0.320	227.0	
41	Tomato	93.1	0.684	136.0	Elongated Tomatoes Specie "Tamar"
42	Soya	28.5	0.645	44.0	
43	Wheat flour	75.8	1.970	38,5	
44	Quaker oats	57.9	0.770	75.2	
45	Millet	51.0	0.707	72.1	"Shefa-On"
46	Beer	20.5	0.200	73.0	"Nesher"
47	Wine	6.28	0.230	30.3	Carmel Misrachi Alicant
48	Wine	6.6	0.290	22.8	Carmel Misrachi Alicant
49	Tamarisk	376.6	0.720	523.0	From "Fibres and forest products Institute"
50	Cotton fibres	32.0	0.594	54.0	One week after harvesting sample No. 2
51	Cotton peel	78.5	1.190	66.0	One week after harvesting sample No. 2
52	Cotton leaves	582.0	7.96	73.0	
53	Cotton fibres	46.4	2.215	21.0	One month after harvesting sample No. 1
54	Cotton peel	96.4	2.57	37.5	One month after harvesting sample No. 1
55	Irrigating water	32.5	0.064	508.0	3.3 miles from Masmiye, road to Beer-Sheva (for irrigation of cotton field)
56	Soil from cotton field	17.0	0.246	69.1	3.3 miles from Masmiye, to Beer-Sheva, 15.12.58
57	Soil from cotton field	7.24	0.57	12.7	3.3 miles from Masmiye, road to Beer-Sheva, 4.4.59

B. INVESTIGATION OF SAMPLES OF HUMAN BLOOD, URINE, SWEAT AND SALIVA

The detailed procedure of the analyses of these specimen has been described by Kaplan and Schnerb (1958). The analyses were carried out with material from the maternity ward of the Shaare Zedek Hospital in Jerusalem and from employees of the Dead Sea Works, Beersheba and Jerusalem. The samples from the Dead Sea Works have been taken under carefully controlled conditions by a team of investigators of the Kupath Cholim (Israel Workers Health Insurance). Other pertinent data have been published by Dr. Toor and co-workers (1957).

Tables III-VI show the result of these investigations.

TABLE III

Serum

Name	Br^- mg/100 ml	Cl^-mg/100 ml	Cl^-/Br^-
*N.S.	0.61	414	680
R.A.	0.96	394	410
*S.R.	0.93	322	346
R.A.	1.5	376	251
S.J.	1.39	397	286
*L.C.	0.78	368	472
*M.M.	0.96	386	402
*Z.L.	0.92	378	411
K.M.	1.0	373	373
*S.M.	1.68	355	211
*S.N.	1.04	352	340
G.J.	1.12	380	339
*P.M.	0.789	373	473
*J.S.	0.65	370	570
*M.G.	0.906	382	422
TC.M.	1.73	366	500
*J.A.	1.43	386	270
*A.G.	1.91	388	195
*M.S.	0.92	382	420
*S.S.	1.00	285	285
*MC.S.	1.35	361	267
*MC.S.	1.07	357	324
*B.	1.82	314	216
*Z.	0.906	423	465
*P.	1.10	355	323
***A.P.	1.42	394	277
**BL.	0.98	363	370
*SL.	1.28	386	306
***AB.	1.73	334	193
*SO.	1.58	422	267
*JL.	1.17	410	350
*JL.	1.19	379	318
*AD.	0.59	334	570
M.B.	0.89	367	410
*F.M.	0.90	381	423

* Urine was sampled simultaneously. ** Sweat and saliva were sampled simultaneously. *** Urine, sweat and saliva were sampled simultaneously.

TABLE IV

Urine

Name	Br^-	Cl^-	Cl^-/Br^-
	mg/100 ml		
N.S.	0.84	940	1119
S.R.	0.84	607	731
Z.P.	0.52	451	867
L.C.	0.61	433	710
M.M.	1.31	818	624
Z.L.	0.70	451	644
S.M.	0.85	644	757
S.N.	0.92	523	568
S.C.	0.74	633	852
F.M.	0.30	266	899
J.S.	0.335	162	483
P.M.	0.265	235	887
G.M.	1.07	677	632
T.Z.	1.48	1042	704
J.A.	0.567	309	544
A.G.	0.25	108	432
M.S.	0.39	283	726
S.S.	0.538	329	610
MC.S.	0.19	92	486
MC.S.	0.22	103	467
B.	0.348	420	1200
Z.	0.887	830	935
P.	0.688	558	815
BU.	2.255	747	2930
M.	1.067	676	635
AP.	1.424	1063	750
SL.	0.628	523	835
AB.	0.507	463	910
SO.	0.970	637	660
ST.	1.143	1368	1200
JL.	1.299	828	635
AD.	1.232	817	665
MS.	1.835	835	455
CM.	0.380	321	845
AJ.	0.650	486	751

TABLE V

Sweat

Name	Br^-	Cl^-	Cl^-/Br^-
	mg/100 ml		
B.	0.71	317.5	447
M.	4.26	1065	250
AP.	4.65	1618	348
BL.	4.99	1206	328
S.	4.4	564	128
SL.	2.7	301	111
AB.	3.0	4616	154
MS.	3.79	644	170
MS.	1.24	212	293
BL.	26.3	4479	170

TABLE VI

Saliva

Name	Br^- mg/100 ml	Cl^-	Cl^-/Br^-
B.	0.82	42.0	51
P.	1.05	69.9	66
BU.	0.82	70.0	85
AP.	0.72	62.8	87
BL.	0.39	40.5	104
AB.	0.67	66.0	98
S.	0.7	50.0	71
L.	0.39	55.0	141
AM.	0.61	69.9	114
AD.	0.29	48.0	165

C. WATER

Water, which sustains life, always contains chloride and bromide. We analysed samples obtained from 19 localities in Israel and from 8 highly populated areas abroad (Table VII).

TABLE VII

Israel (During 1957)	$Cl^- + Br^-$ ppm	Cl^-/Br^- (weight ratio)	Other countries (January-March 1957)	$Cl^- + Br^-$ ppm	Cl^-/Br^- (weight ratio)
Jerusalem	161	280	London	34	250
Jordan river	300	100	Birmingham	12	350
Tel-Aviv	121	350	N.Y.	4	90
Beersheba	151	380	Vienna	4	90
Dead Sea Works (South)	370	380	Zurich	5	50
Ramat Gan	46	170	Rome		120
3.3 miles south from Masmieh	32	508	Amsterdam	65	360
Mahanaim	28	130	den Haag	94	500
Beth Sera	330	125			
Ein Harod	504	245			
Tirath Zvi	160	248			
Gewa Hacarmel	78	294			
Hibath Zion	64	310			
Kfar Yedidia	113	320			
Beth Yizhak	186	377			
Ein Zurim	119	365			
Yarkon-Negev line	172	308			
Askelon	253	550			
Bizath	155	288			

The results are similar to those found by other authors (Selivanoff 1944, Yaron and Heitner 1952, d'Ans and Kühn 1940). Oceanic water has a ratio of Cl^-/Br^- 300

(Dittmar, 1884). Consequently, all drinking water and irrigation water derived from sources originating in marine deposits can be expected to have a ratio near 300. Other rocks mostly have a lower ratio.

D. COMMON SALT (NaCl)

The most important source of halogens in the human diet is common salt, used as a condiment and food preservative with almost every kind of food. Consequently, it seems to us of great significance that the chloride-bromide ratio in common salt differs from that in all other food by an order of magnitude.

In crystallised NaCl (rock salt, sea salt, salt from brines) a ratio of several thousand parts chloride to one part bromide is found (Cl^-/Br^- 2000 to 16,000) (d'Ans and Kühn 1940, Bloch and Schnerb 1953, Haslam, Allberry and Moses 1950). The explanation for these characteristic ratios is that whereas oceanic water contains chloride and bromide ions in a constant ratio of Cl^-/Br^- 300, solid common salt derived by crystallisation from oceanic water or from any other brine contains much more chloride per bromide than the mother liquor from which it has crystallised. NaCl and $NaBr \cdot 2H_2O$ do not form mixed crystals (Boeke 1908). By evaporating oceanic water to the concentration point where the first traces of NaCl precipitates, salt is found with a ratio of Cl^-/Br^- 16,000. When, after further evaporation, all edible salt is precipitated, the last such salt to precipitate has a ratio of Cl^-/Br^- 2000. This corresponds to 300 ppm bromine and represents the highest bromide content normally occurring in table salt.

E. CORRELATION OF Cl^-/Br^- RATIO IN FOOD AND BODY FLUIDS

We will now consider the probable ratio of chloride to bromide in human food and consequently in the liquids of the human body.

It is to be expected that the Cl^-/Br^- ratio of food is somewhere between a minimum of 50 for a diet which contains no common salt and a maximum of several thousand when the prevalent chloride intake is in the form of common salt. The more common salt is consumed the higher will the ratio be. If we assume, for example, that 15 g salt are consumed per day, 5 g of it in food, water etc. (Cl^-/Br^- 300) and 10 g as common salt (Cl^-/Br^- 2000), the average Cl^-/Br^- ratio for the whole halogenide intake is about 700.

Since most of the chloride and bromide consumed can be expected to leave the human body via the kidneys, it can be assumed that for steady state conditions the Cl^-/Br^- ratio in urine equals the ratio found in food and drink and that it varies with it. This is true only when sweat and faeces contain little halogenide compared with the urine, a reasonable assumption under normal circumstances, but not tenable for pathological conditions and for very hot climates.

In social groups where no solid salt is added to the food (this is the case practically only with very primitive hunting, fishing and cattle-raising nomads) the Cl^-/Br^-

ratio in food will be around 300 or lower and this ratio will also prevail in the urine of such people. Agricultural communities normally supplement their diet with solid salt (Clag Trumbull 1899, Bloch 1953, Kaunitz 1956, Ladell 1957) hence the average Cl^-/Br^- ratio in their food, and consequently also in their urine, will be much higher than 300. The ratio might rise to several thousand when a lot of rock salt NaCl is eaten (Damiens 1920).

Our knowledge of the Cl^-/Br^- ratio in food, drinking water and rock salt NaCl does not allow any prediction about the Cl^-/Br^- ratio of any liquids in the human body, other than urine. The Cl^-/Br^- ratio in blood, lymph, saliva, sweat, gastric juices, tears, secretions like those of the liver, the sexual glands and in milk, cannot be deduced from these data; these ratios have to be determined directly.

Table VIII gives the maximum and minimum ratios as well as the ratios calculated from average analyses.

TABLE VIII
(Cl^-/Br^- weight ratio

	Maximum	Minimum	Average	No. of persons
Serum	570	190	332	35
Urine	2900	450	750	35
Sweat	450	107	267	10
Saliva	165	50	89	10

It is significant that the extraordinary high ratio of Cl^-/Br^- (570) in serum occurred when the urine of the same person at the same time showed a Cl^-/Br^- ratio of 672, which approximates the average for urine. On the other hand, a nearly average Cl^-/Br^- ratio (265) in serum occurred simultaneously with a very high Cl^-/Br^- ratio (2900) in urine.

The average value of 330 for Cl^-/Br^- in blood conforms to earlier published data of the bromide content in blood. (Zondek and Bier 1932, Karp and Wolfsohn 1939, Wikoff et al. 1940, Bernhardt and Ucko 1926). Our results show that although the Cl^-/Br^- ratio in the nutrients consumed might be very high (deduced from urine analysis) the ratio remains low in blood. The kidney seems to work as an efficient bromide retaining organ; the halogenides reabsorbed in the tubule of the kidney are much richer in bromide than those in the filtrate from which the urine is formed. This is in agreement with the experimental data of Mason (1936) who found that when feeding bromide, the latter was retained in the serum for a considerable time.

How far this regulating mechanism of the kidney counterbalances extreme fluctuations of common salt content in the diet should be more exactly investigated. It is quite probable that the use of common salt, characteristic for peoples of agricultural civilizations, has somewhat lowered the bromide content of their blood.

Samples of sweat from persons living under conditions prevailing in summer were found to have a Cl^-/Br^- ratio lower than that found in their blood-serum. By excessive sweating, a lot of bromide is lost. If in the case of excessive sweating the Cl^-/Br^- ratio in the blood is to remain below a certain level, some mechanism must be operating which further enhances the tendency of the tubule of the kidney to reabsorb Br^- preferentially to Cl^-. This regulating mechanism which keeps the bromide content of blood-halogenide above a certain level is superimposed on the mechanism which keeps the halogenide content of blood as a whole constant.

Saliva has been found to have a surprisingly low Cl^-/Br^- ratio (Table III). This is in keeping with the findings of Mason who showed that when feeding bromide, the saliva becomes exceedingly rich in bromide (1936).

Zondek (1931–1932) was the first to show that under normal conditions the human blood contains a relatively constant amount of bromide and that exceptionally low bromide content in blood is connected with certain pathological mental conditions. Lately, Huff, Bosshardt, Miller and Barns (1956) showed that a bromine-deficient diet for mice and chicken might retard growth. Since feeding animals on a completely bromide-free diet is very difficult, as all plants seem to have a very high bromine content, we are planning to raise bromide-free plants for such experiments.

F. CONSLUSION

1. Plants have a high bromide content in their halogenides (low Cl^-/Br^- ratio), even when the water with which they are irrigated has a relatively low bromide content (high Cl^-/Br^- ratio.)
2. Any salt-free diet has a relatively high bromide content.
3. Salt (NaCl) used as condiment, having very little bromide to chloride, very much reduces the relative bromide content of the halogenides in foods.
4. The bromide content of urine halogenides is always lower than that of blood-serum (about twice as low). The kidney reabsorbs bromide preferably to chloride.
5. Sweat and saliva have a higher bromide content in their halogenides than blood and urine. Sweating makes the human body lose more bromide than chloride, counteracting the reverse effect of the kidneys.

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THE MECHANISM OF THE HYDROLYSIS OF BROMINE*

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ABSTRACT

Experiments on the rate of hydrolysis of bromine at various values of *p*H are described, using the continuous flow method. Lower limits for the rate constants corresponding to various possible mechanisms were obtained. These values are compared with the number of encounters between reactants in solution .Thus certain mechanisms can be ruled out, whereas others are shown to be compatible with the experimental results.

INTRODUCTION

The investigation of the hydrolysis of the halogens offers the possibility of gaining insight into the mechanism of a chemical reaction in which a homonuclear molecule, which possesses no permanent dipole moment, interacts with a dipolar solvent, water, yielding ionic products. There arises the question of the possible mechanisms and their respective velocities.

The hydrolysis of chlorine in pure water has been investigated[1], and the result discussed by Morris[2] who concludes the rate determining step to take place between Cl_2 and OH^-, although this leads to an extremely high value for the rate constant.

The hydrolysis of bromine has not been investigated previously. A mechanism involving dissociation of the bromine molecule into two ions has been proposed by Hinshelwood[3]. The rate of exchange of oxygen between H_2O^{18} and HOX in strongly alkaline solution has been investigated by Anbar and Taube[4]; this exchange is likely to proceed *via* molecular halogen[5]. Evidence for a reaction involving HOBr and Br^- in the rate-determining step was obtained by these authors.

In the present work, a direct measurement of the rate of hydrolysis of bromine has been attempted.

APPARATUS

The continuous flow method of Hartridge and Roughton[6] was employed, the extent of reaction being measured by the thermal method[6]. The temperature gradient along the reaction tube was measured by 5 thermistors placed at suitable intervals. The apparatus, which gives satisfactory results for reactions having half-times of about 10^{-2} sec, and heat effects of about 0.1°C or more, is described elsewhere[7]. The temperature in all experiments was 25°C.

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RESULTS

The equilibrium constant for the reaction:

$$Br_2 + H_2O \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} HBrO + Br^- + H^+ \tag{1}$$

is very low ($K_1 = 5.8 \times 10^{-9}$ at 25°C[8]), and therefore the reaction takes place to an extent measurable in our apparatus only when the equilibrium is shifted to the right by the addition of suitable reagents.

In the first series of experiments, this was achieved by mixing bromine water with a buffer solution of Na_2HPO_4 and NaH_2PO_4, thus decreasing the concentration of H^+. The extent of reaction was about 10%, and was calculated at each pH from the equilibrium constant of reaction (1), and the stoichiometric concentration of bromine in the reaction mixture (approximately 6×10^{-2} M). From this, together with the values of ΔH (calculated from the dependence of the equilibrium constants on temperature[8,9]: $\Delta H_1^\circ = 13.4$ Kcal mole^{-1}, $\Delta H_{\text{buffer}}^\circ = -0.97$ Kcal mole^{-1}) the expected rise in temperature was calculated; the agreement with the experimental value (approximately 0.08°C) was satisfactory. However at pH 6.8, 5.9 and 5.3, and a flow-velocity of 350 cm sec^{-1}, equilibrium was attained, within the limit of experimental error, by the time the first thermistor was reached, *i.e.* after 3.8 milliseconds.

A second series of experiments was carried out at $p\text{H} = 1$, where equilibrium (1) can be shifted to the right by decreasing the concentration of *bromide*. This was achieved by mixing 7×10^{-2} M bromine water with a 2.9×10^{-2} M solution of $Hg(NO_3)_2$, both reactants having been brought to $p\text{H} = 1$ by the addition of nitric acid.

The dissociation constant of $HgBr_2$ into Hg^{++} and bromide ions is very low* and the amount of bromine hydrolysed at equilibrium is almost equivalent to the stoichiometric concentration of the mercuric salt (under our conditions of pH and concentrations the difference is 2.6%).

At $p\text{H} = 1$, again, the reaction was virtually complete at the first thermistor, *i.e.* after 5.5 milliseconds.

DISCUSSION

From our measurements, only a lower limit for the reaction velocity can be calculated. We shall assume — rather arbitrarily — that the reaction has gone at least 95% towards equilibrium when the mixture reaches the first thermistor, and calculate on this basis *lower limits* for the rate constants corresponding to various mechanisms. In this way, we cannot conclusively *prove* a certain mechanism to be correct, but we can *rule out* any mechanism which leads to an impossibly high value for the corresponding rate constant. — The upper limit for a second-order rate constant in solution will be assumed equal to the number of encounters per second which is estimated to be about 5×10^{10} for a reaction between H^+ or OH^- and another ion of opposite sign. (For all other reactions it is lower)[10,11,12].

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* $K_D = [Hg^{++}][Br^-]^2/[HgBr_2] = 4.8 \times 10^{-18}$ (O. Bethge, I. Jonevall-Westöö and L. G Sillén, 1948, *Acta Chem. Scand.*, **2,** 828.

Let us first consider the case where equation (1) represents the mechanism. For the hydrolysis in buffer solution the corresponding rate equation yields on integration

$$kt = (1/B)\ln[(1 + B + Ax)/(B - 1 - Ax)] \qquad \text{(I)}$$

$$\text{where} \quad A \equiv [H^+]/K_1 \qquad B \equiv (2aA + 1)^{\frac{1}{2}}$$

with k equal to k_1, a designating the stoichiometric concentration of bromine in the reaction mixture, and x the amount hydrolysed at time t. The amount hydrolysed at zero time can be neglected.

For the hydrolysis by Hg^{++} in acid solution we calculate k_1 from a simple first-order rate equation, *i.e.* we neglect the back-reaction. The error thus introduced is less than 20%, which is sufficient for our purposes.*

Inserting numerical values into expression I, with $x = 0.95x_{\text{equilibrium}}$, we obtain for the lower limit of k_1 values between 60 to 130 $\sec^{-1}$ (according to pH) which leads to values of k_1' between 10^{10} to 2×10^{10}. In order to explain the rate of hydrolysis in acid solution we must assume still higher values for the rate constants, namely $k_1 = 500$ and $k_1' = 10^{11}$.

Now, k_1' corresponds to a reaction between three partners. If it is a true third-order constant, its upper limit will probably lie *below* that of a second-order constant. If the reaction occurs in stages, k_1' will be the product of a second-order constant and the association constant of either H_2BrO^+ which is very low[13], or $HOBr_2^-$ which has not been measured, but which would seem unlikely to be considerably higher than unity**. Hence, the upper limit of k_1' is either lower than, or possibly equal to, that of a second-order constant. Comparing this value with the lower limits for k_1' obtained by us, we may conclude that *for the hydrolysis in buffer solution mechanism* (1) *is extremely unlikely, and for the hydrolysis in acid solution it can definitely be ruled out.*

Let us now discuss the possibility of the following process being rate determining:

$$Br_2 + OH^- \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} HOBr + Br^- \qquad (2)$$

In all our experiments, the hydroxyl ion concentration is much lower than that of bromine. Therefore, after a very small percentage of reaction has taken place, reaction

---

* The full rate-equation is $dx/dt = k_1 \{(a-x) - [H^+][Br^-]x/K_1\}$ where $[Br^-]$ is obtained from $[Br^-] = [K_D x/(2c - x)]^{1/2}$ with c representing the stoichiometric concentration of Hg^{++}. The second member in parenthesis changes from a negligibly small value at the beginning of the reaction to $0.13x$ when 95% equilibrium has been attained.

** Anbar, Guttmann and Rein[5] explain the high rate constant for the chlorine exchange between HOCl and Cl^- (which is faster than the hydrolysis of chlorine) by assuming a dissociation constant of unity for $HOCl_2^-$ into Cl^- and HOCl.

(2) cannot proceed faster than hydroxyl ions are supplied. On the other hand, we know from experiments that the rate of reaction[*] is at least 2 mol l^{-1} sec^{-1}.

Now, in the experiments in acid solution, the ionisation of water is the only possible source of hydroxyl ions. But this reaction takes place[10] at a rate of 1.5×10^{-3} mol l^{-1} sec^{-1} *i.e.* it is far too slow to supply OH^- at the necessary rate, and *mechanism* (2) *is therefore ruled out for the hydrolysis in acid solution.*

In buffer solution it is possible[14] that the hydroxyl ions be supplied directly by the reaction

$$A^- + H_2O \underset{k'_3}{\overset{k_3}{\rightleftharpoons}} HA + OH^- \tag{3}$$

where HA and A^- stand for the buffer acid and its anion, respectively ($H_2PO_4^-$ and $HPO_4^=$ in our case).

As far as we are aware, the rate of reaction (3) has not been measured. If it were fast enough for equilibrium (3) to remain undisturbed by reaction (2), the rate equation would again yield expression I on integration, with $k = k_2[OH^-]$. Integration between the same limits as before would yield $k_2 \geqq 3 \times 10^{10}$ and 1.6×10^{10}, and $k'_2 \geqq 5 \times 10^4$ and 2.8×10^4 from results at *p*H 5.3 and 5.9 respectively. However, a rather crude estimate[**] shows that k_3 cannot be higher than about 2×10^3 sec^{-1}. In this case reactions (2) and (3) may proceed at comparable rates, and $[OH^-]$, calculated from the steady-state hypothesis, is lower than the equilibrium value corresponding to (3). This fact calls for still higher values of k_2 to explain the observed velocity, so that the above values constitute a lower limit of a lower limit.

Summarising, we might say that our values for k_2 are so high as to be almost prohibitive and *it seems extremely unlikely that the hydrolysis in buffer solution at our values of pH should proceed by mechanism* (2).

This conclusion does not preclude the possibility that in more alkaline solution the reaction proceeds *via* mechanism (2). From Anbar and Taube's data in alkaline solution[4] we calculate $k_2 = 1.9 \times 10^9$ mol^{-1} l sec^{-1}. If this represents the rate of hydrolysis, reaction (2) becomes predominant over the reaction schemes proposed below already at *p*H $\geqq 7$.

Another possibility for the mechanism of the reaction in buffer solution consists in a direct attack of the buffer anion (in our case $HPO_4^=$) on the bromine molecule. This anion may either abstract a proton from the hydrated bromine molecule (in analogy with reaction (3)), according to

---

[*] In acid solution, 1.3×10^{-2} mol l^{-1} react in 5.5 millisec., or 2.5 mol l^{-1} sec^{-1}; in buffer solution, *e.g.* at *p*H 5.3, 0.72×10^{-2} mol l^{-1} react in 3.8 millisec., or 1.9 mol l^{-1} sec^{-1}. — The rate of reaction during the initial stage of the reaction is of course faster.

[**] The equilibrium constant of reaction (3) is 1.3×10^{-7}; if we assume the back reaction to proceed at the highest rate possible for a reaction between OH^- and a molecule, (say $k'_3 = 1.5 \times 10^{10}$) we get as an approximate limit: $k_3 = 2 \times 10^3$.

$$\left.\begin{array}{llll} Br_2.HOH + A^- & \longrightarrow & HOBr_2^- + HA & \text{(measurable)} \\ HOBr_2^- & \longrightarrow & Br^- + BrOH & \text{(fast)} \end{array}\right\} \quad (4)$$

Alternatively, the anion may polarise the bromine molecule and in the rate-determining step break the covalent Br-Br bond, while forming another covalent bond with one of the fragments, the other fragment carrying away the charge:

$$\left.\begin{array}{llll} \overset{\delta-}{Br} - \overset{\delta+}{Br} + A^- & \longrightarrow & Br^- + BrA & \text{(measurable)} \\ BrA + H_2O & \longrightarrow & BrOH + HA & \text{(fast)} \end{array}\right\} \quad (4a)$$

The reaction with OH^- at higher values of pH falls in line with the first step of mechanism (4a), and leads to a mechanism somewhat similar to that proposed by Hinshelwood[3], though involving a *bi*molecular rate determining step.

Substances of the type ABr and the analogous chlorine compounds are discussed by Anbar and Ginsburg[15], and have been assumed as unstable intermediates in halogenation reactions by hypohalous acids[16,17].

The rate constants corresponding to mechanism (4) and (4a) can be obtained by substituting $k = k_4 [A^-]$ in expression I; the values of $[A^-]$ were around 0.1 *M*. Reasonable values for both k_4 and k'_4 are obtained.

In the hydrolysis in strongly acid solution, the cations Hg^{++} and $HgBr^+$ can act in a similar way, abstracting Br^- and leaving H_2BrO^+ which is known to break up into HOBr and H^+:

$$\left.\begin{array}{llll} H_2O.\overset{\delta+}{Br} - \overset{\delta-}{Br} + Hg^{++} & \longrightarrow & H_2BrO^+ + HgBr^+ & \text{(measurable)} \\ H_2BrO^+ & \longrightarrow & H^+ + HBrO & \text{(fast)} \end{array}\right\} \quad (5)$$

with an analogous reaction between bromine and $HgBr^+$.

The integration of the rate-equation will be simplest if we arbitrarily assume the rate-constant for Hg^{++} to be twice that for $HgBr^+$; in any case, very reasonable values for k_5 and k'_5 are obtained.

Summarising, we may say that the mechanism of the hydrolysis of bromine changes with changing conditions. The unimolecular splitting of the bromine molecule — possibly under the influence of the dipoles of the surrounding water molecules — will always make *some* contribution to the reaction rate, but in the presence of a suitable acceptor for a positive or negative ion the reaction will be much faster.

It is interesting to note that these acceptors do not shift the hydrolytic equilibrium in the ordinary way by decreasing the concentration of one of the products, but do so directly by increasing the rate of the *forward* reaction. Preliminary results obtained for the hydrolysis of chlorine in pure water and in buffer solutions confirm the conclusions reached in the present paper.

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THE REARRANGEMENT OF 9,10-DI-(HYDROXYMETHYL)-9,10-DIHYDROANTHRACENE TO A DIBENZOCYCLOHEPTATRIENE DERIVATIVE

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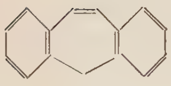
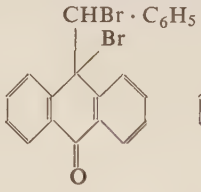
ABSTRACT

The bis-*p*-toluenesulfonate of 9,10-di-(hydroxymethyl)-9,10-dihydroanthracene (IV) is solvolysed by formic acid to l-hydroxmethyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (VII).

The preparation of 2,3,6,7-dibenzocyclohepta-2,4,6-triene (I) and its derivatives is fairly cumbersome[1–3]; for the preparation of larger quantities shorter routes were, therefore, explored. The observation of Cook[4] that the dibromide (II) of benzylideneanthrone reacts with silver oxide in aqueous acetone to give 4-phenyl-2,3,6,7-dibenzocyclohepta-2,6-diene-1,5-dione (III) led us to study the solvolysis of esters of 9,10-di-(hydroxymethyl)-9,10-dihydroanthracene (IV). An analogous investigation has very recently been reported by Rigaudy and Tardieu[5].



I



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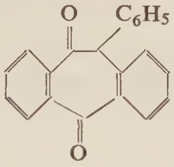

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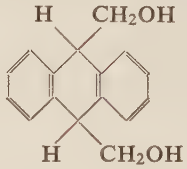

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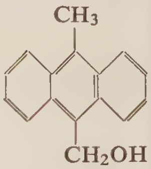

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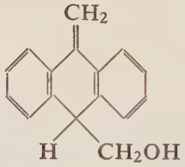
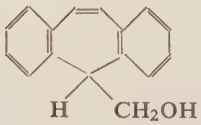


VI



VII

The dialcohol (IV) was prepared by lithium aluminum hydride reduction of the corresponding 9,10-dihydroanthracene-9,10-dicarboxylic acid; the *cis*-form of the acid was used[6–8].

The bis-tosylate of (IV), upon solvolysis with boiling formic acid, gave in 40% yield a compound of m.p. 88° (after hydrolysis), which did not fluoresce and was, therefore, not 9-methyl-10-hydroxymethyl-anthracene (V) (this would have formed

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spontaneously from 9-methylene-10-hydroxymethylene-9,10-dihydroanthracene (VI))[9,10]; the alternative formula of 1-hydroxymethyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (VII) was supported by the ultraviolet spectrum which resembles closely that of *cis*-stilbene:

VII: 288 mμ (log ε 4.19)
cis-stilbene: 280 mμ (log ε 4.10)

EXPERIMENTAL

cis-9,10-*Di-(hydroxymethyl)*-9,10-*dihydroanthracene* (*IV*)

At the temperature of an ice-salt mixture, 8 g of lithium aluminum hydride was added, slowly and with efficient agitation, to a suspension of 30 g of *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid in 500 ml. of dry ether. The mixture was refluxed for 8 hours and decomposed as usual, and the ether evaporated. Thus, 17 g (60%) of a colourless substance was obtained which melted, after recrystallisation from benzene, at 166–167°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.6. Found: C, 80.5; H, 6,5.

Bis-tosylate. To 10 g of (IV) in 70 ml of pyridine, 16 g of *para*-toluenesulfonyl chloride was added at 0° in small portions and the mixture kept at this temperature for 48 hours. Then the product was poured onto ice and the solid filtered and washed with methanol. From butanol, the di-tosylate of (IV) formed colourless crystals of m.p. 185–187°. Yield, 18 g (70%).

Anal. Calcd. for $C_{30}H_{28}O_6S_2$: C, 65.7; H, 5.1. Found: C, 65.7; H, 5.2.

1-*Hydroxymethyl*–2,3,6,7-*dibenzocyclohepta*-2,4,6-*triene* (*VII*)

A mixture of 5 g of the foregoing compound and 100 ml of anhydrous formic acid was refluxed for 6 hours and slowly poured into an excess of sodium carbonate solution. The organic product was refluxed for one hour with 25 ml of alcoholic potassium hydroxide solution (10%), neutralised with acid and extracted with ether. The mono-alcohol (VII) was purified by chromatography and recrystallised from cyclohexane or petroleum ether; it melted at 88°. Yield, 2 g (40%).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.4. Found: C, 86.7; H, 6.4.

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THE DEHYDRATION PROPERTIES OF SOME HYDRATED RARE EARTH OXALATES, AND THE EXCEPTIONAL BEHAVIOUR OF CERIUM (III) OXALATE

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ABSTRACT

Lanthanum, cerium (III), samarium and other rare earth oxalates may be dehydrated at 320° in *vacuo* without decomposition. In air, cerium (III) oxalate is converted at this temperature into cerium dioxide. None of the other rare earth oxalates behave in this manner. The exceptional behaviour of cerium (III) oxalate as well as the similar behaviour of plutonium (III) and americium (III) oxalates, are attributed to the susceptibility of these trivalent cations to oxidation to the quadrivalent state.

The rare earth oxalates are known to crystallize with ill defined amounts of water of crystallization, mostly with 8 to 11 mols of H_2O per formula weight of the oxalate [$Ln_2(C_2O_4)_3.nH_2O$, where Ln symbolises any member of the lanthanide series]. Attempts to prepare the anhydrous salts were unsuccessful, e.g. Wylie[1], on heating some of the hydrated oxalates at 180° in *vacuo*, obtained solids that retained about 8% of their original water contents.

Some information on the thermal dehydration and decomposition of the hydrated rare earth oxalates in air was obtained by the thermogravimetric method[2,3]. The thermograms indicated that only a few of the anhydrous salts would be stable.

As a preliminary to a study of the thermal decomposition of the rare earth oxalates in this laboratory, the hydrated oxalates were dried at about 300° in *vacuo*. It was found that this temperature was suitable for a practically quantitative dehydration of the light rare earth oxalates, including cerium (III) oxalate, without causing further decomposition. The europium (III) salt behaved in a different manner and will be dealt with elsewhere.

When the hydrated oxalates were heated in air, the lanthanum and the samarium salts were found to behave as in *vacuo*, but the hydrated cerium salts decomposed further under these conditions, in agreement with observations of earlier workers[1-3].

EXPERIMENTAL

The oxalates were prepared from pure oxides (99.9 %, Lindsay), except the cerium (III) oxalate, which was prepared from pure cerium (III) nitrate. In some

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experiments, cerium oxalate supplied by Lindsay (code 225) was used, with identical results. The oxalates were precipitated from nitric acid solutions as described elsewhere[4]. The oxide content of the preparations was determined by titrating the oxalate with permanganate. For the evaluation of the cerium salt a modified method had to be developed[5].

The behaviour of the oxalates on heating was observed:

(a) in *vacuo*, the temperature being kept constant (± 0.1°C) by a Fielden electronic regulator,

(b) in air, using a Stanton thermobalance.

Pressures in the experiments in *vacuo* were measured with a calibrated McLeod, and simultaneously read on a "Televac" (Fredricks and Co.).

In order to obtain qualitative information on the composition of the dehydrated solids, infrared absorption spectra were measured, using a Baird infrared spectrophotometer, by the potassium bromide pellet method.

RESULTS

Oxalates, partly dehydrated at 180°C, of lanthanum, cerium (III), praseodymium, neodymium, samarium and gadolinium were heated in *vacuo* (1 μ pressure) at gradually increasing temperatures. The samples were kept at the predetermined temperature for at least four hours in each case. The evolved water vapours were condensed in a carbon dioxide-acetone trap, so that after a short rise, the pressures returned to their initial values, if no other gases were produced. It has been established that up to 320°C, no permanent rise in pressure occurs with any of the oxalates mentioned above.

The loss in weight of the sample was found equal to the water content of the hydrate, which was determined both by titration with permanganate, and by calcination at 900°–950° in a muffle furnace. For example, the actual values obtained with a sample of cerium (III) oxalate hydrate were as shown in Table I.

TABLE I

Percentage of H_2O *in a sample of* $Ce_2(C_2O_4)_3.nH_2O$

Water content by:—	
calcination at 950°, assuming quantitative conversion to CeO_2	20.5%
titration; sample No. 1	20.8%
sample No. 2	22.0%
Loss in weight at 320° in *vacuo**	21.3%

* The same percentage of H_2O was obtained from the gain in weight of an anhydrone tube interposed to absorb the water vapours.

Qualitative evidence that at 320° no further decomposition of the oxalate had taken place was obtained from the infrared spectra of the dehydrated solids, in which the oxalate bands were prominent (Figure 1a), whilst the characteristic absorption bands for carbonate[6], observed in samples decomposed at higher temperatures, were absent. (Table II).

TABLE II

Some prominent infrared absorption bands observed in residues of hydrated cerium (III) oxalate after heating at the temperatures indicated

°C	Wavelengths in μ			
320	2.95*	6.28 (s.)	7.6 (v.s.)	12.7 (v.s.)
375, 391 410	2.95*	7.2 (s.)	—	11.95 (s.)

* due to H_2O absorbed by the KBr powder.
s = strong; v.s. = very strong.

In the case of a single sample of samarium oxalate, which was heated for 27.5 hours in *vacuo* at 320°C, a diffuse band at 11.9 μ, characteristic of the carbonate ion, was observed in the infrared spectrum. This finding was corroborated by a final rise in pressure of 2 μ in the vacuum experiment (corresponding to a conversion of 1–2% to carbonate).

On heating the hydrated oxalates on the Stanton thermobalance in air at 320° (± 2°), it was found that the loss in weight of the lanthanum as well as of the samarium oxalate corresponded to the water content of their respective hydrates. The residue, which did not react to tests for carbonates, was proven to be an oxalate.

Cerium (III) oxalate, on the other hand, decomposed to yellow ceria (CeO_2) as identified by: a) its colour, b) loss in weight of the sample (49.7% at 950° and 48.8% at 320°), c) the infrared spectrum of the solid residue (see Figure 1b), showing a very broad band at 3 μ characteristic of CeO_2, whilst the absorption bands due to the carbonate and the oxalate ions were absent.

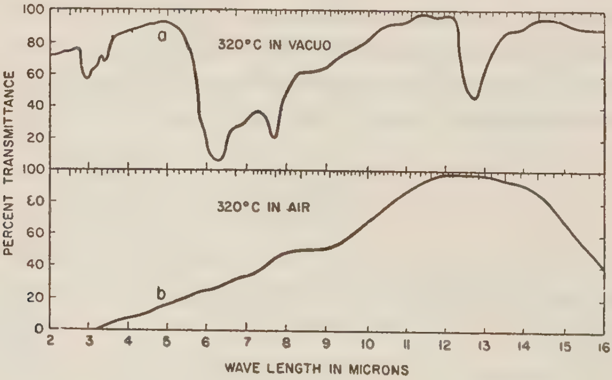

Figure 1

Infrared absorption curves of solid residues obtained after heating $Ce_2(C_2O_4)_3 . nH_2O$ at 320°
a) in *vacuo* b) in air

Cerium dioxide was also produced on heating hydrated cerium (III) oxalate in air at 300°, i.e. this oxalate does not behave in air as in *vacuo*. None of the other rare earth oxalates tested showed similar differences in behaviour.

The low stability of cerium (III) oxalate in air as compared to the other rare earth oxalates has been known previously.

The thermograms given in Figure 2 show that the last traces of water of crystallization are expelled rather slowly, but as soon as this has been accomplished there is an abrupt change in the slope of the curves. In the case of cerium (III) oxalate the final plateau is attained after a comparatively short heating period but with the other rare earth oxalates, decomposition is rather slow, and the formation of the oxide is attained only after two or more intermediate stages. (The temperatures at which brakes in the slope of the thermograms occur are known to be dependent on the rate of heating).

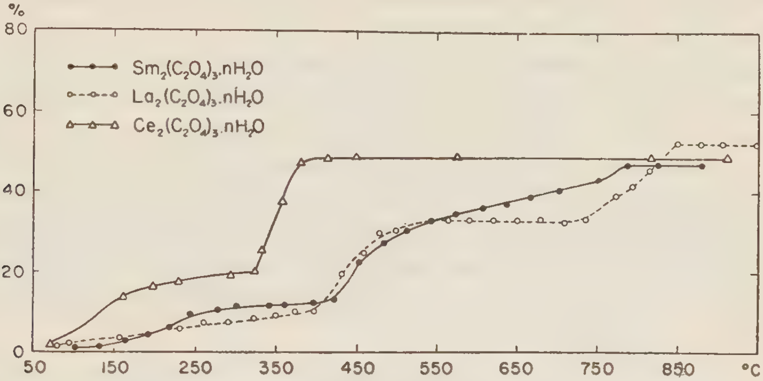

Figure 2

Thermograms showing % loss in weight vs. temperature of hydrated oxalates (in air)

DISCUSSION

It has been shown that the hydrated oxalates of lanthanum, cerium (III) and samarium can be dehydrated (to a large extent, if not completely) at 320° in *vacuo*, without any appreciable decomposition of the oxalates. Similar observations have been made on the oxalates of praseodymium, neodymium and gadolinium. The dehydration of erbium and lutecium oxalates, under these conditions, is less complete whilst with europium (III) oxalate, decomposition occurs even at a much lower temperature.

The behaviour of the rare earth oxalates in air is very much the same as in *vacuo* with the exception of cerium (III) oxalate. This last salt decomposes in air with simultaneous oxidation to CeO_2, hence cerium (III) oxalate should be dried in air at a temperature below 260°.

It is of interest to mention here some similar phenomena observed with the oxalates of the transuranium elements. Plutonium (III) oxalate[7] decomposes to PuO_2 when heated in air at 400°, but the oxide is formed in vacuum only on heating the sample to 850°. On the other hand, plutonium (IV) oxalate decomposes to plutonium dioxide at 400° in less than twenty minutes, in *vacuo* as well as in air.

Similar results have been recorded by Russian workers[8], but no explanation has been offered for the difference in behaviour of plutonium (III) oxalate in air and in its absence.

The thermograms of americium (III) oxalate also show the latter to behave differently when heated in air than when heated in *vacuo*[9].

This anomalous behaviour of the three cations mentioned is evidently due to their susceptibility to oxidation in air to the quadrivalent state. Oxidation of the cation, which takes place before decomposition, is accompanied by a decrease in the thermal stability of the resulting salt of lower basicity. This is most evident in the case of plutonium, o which both the trivalent and the quadrivalent oxalates are known. On the other hand, although samarium occupies a position in the lanthanide series corresponding to that of plutonium in the actinide series, it has no tendency to be oxidized to the quadrivalent state, hence samarium (III) oxalate exhibits the same stability in air as in *vacuo*.

In *vacuo*, or in an inert non-oxidizing atmosphere, the oxalates of the trivalent cations of cerium, plutonium and americium are more stable than in air. The stability of cerium (III) oxalate in *vacuo* was demonstrated in this work, cerium thus falling in line with its neighbours in the lanthanide series. Thus cerium (III) oxalate may also be dehydrated in vacuum at 320°; when heated above this temperature, it yields a number of intermediate compounds before its complete decomposition to an oxide[10].

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THE KINETICS AND MECHANISMS OF CARBONYL-METHYLENE CONDENSATIONS X. THE PIPERIDINE CATALYSED REACTION OF AROMATIC ALDEHYDES WITH *p*-NITROBENZYL CYANIDE

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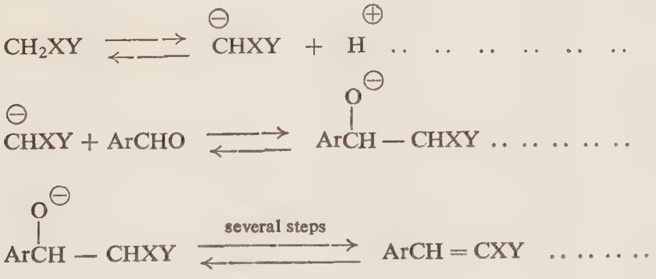
ABSTRACT

The reaction rates of *p*-nitrobenzyl cyanide with piperonal, anisaldehyde, *p*-tolualdehyde, benzaldehyde, *p*-chloro-, *o*-chloro- and *p*-nitro-benzaldehyde were measured at different concentrations, in the presence of differing amounts of piperidine as the catalyst. The reaction has a first order dependence on the catalyst concentration. With constant piperidine concentration, intermediate reaction orders (between first and second) were observed for the overall rate. The mechanism of the reaction is discussed.

INTRODUCTION

In previous papers of this series, we investigated the kinetics and the mechanisms of various carbonyl-methylene condensations, between different aromatic aldehydes and a number of active methylene compounds, such as malononitrile, ethyl cyanoacetate and cyanoacetamide[1]. From the results obtained using ethanol or water as the reaction medium in the absence of catalysts, we proposed a general reaction mechanism consisting of the following main steps:



$$\mathrm{CH_2XY} \rightleftharpoons \overset{\ominus}{\mathrm{C}}\mathrm{HXY} + \overset{\oplus}{\mathrm{H}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\overset{\ominus}{\mathrm{C}}\mathrm{HXY} + \mathrm{ArCHO} \rightleftharpoons \mathrm{Ar}\overset{\overset{\mathrm{O}^{\ominus}}{|}}{\mathrm{C}}\mathrm{H}-\mathrm{CHXY} \quad \ldots\ldots\ldots \quad (2)$$

$$\mathrm{Ar}\overset{\overset{\mathrm{O}^{\ominus}}{|}}{\mathrm{C}}\mathrm{H}-\mathrm{CHXY} \xrightleftharpoons{\text{several steps}} \mathrm{ArCH}=\mathrm{CXY} \quad \ldots\ldots\ldots \quad (3)$$

According to the relative velocities of the three main steps, we obtained overall first order reaction rates in the case when step (1) was the slowest one, and second order rates when step (1) was fast, giving the dissociation equilibrium immediately on the dissolution of the active methylene compound in the solvent.

The purpose of the present paper was to study a condensation reaction which is too slow to measure without a catalyst, and to determine whether the proposed

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mechanism does hold, with the introduction of the appropriate changes, also in the case of a base-catalysed reaction. The reaction chosen was the condensation of aromatic aldehydes with *p*-nitrobenzyl cyanide in ethanol, in the presence of piperidine as the catalyst.

RESULTS

The initial rates of the condensation of various aromatic aldehydes with *p*-nitrobenzyl cyanide in ethanol, in the presence of piperidene, were determined at different concentrations of the reactants and of the catalyst. The results are given in Table I, where both first and second order rate constants are tabulated.

TABLE I

Initial rates (k_1 in sec^{-1}, k_2 in mole^{-1}sec^{-1}) of the reaction of p-nitrobenzyl cyanide (NBC) with piperonal (PA), anisaldehyde (AA), p-tolualdehyde (TA), benzaldehyde (BA), p-chlorobenzaldehyde (pCA), o-chlorobenzaldehyde (oCA) and p-nitrobenzaldehyde (pNA) in ethanol

Run No.	NBC mole l^{-1}	Aldehyde mole l^{-1}	Piperidine mole l^{-1}	T°C	10^6k_1	10^4k_2
P1	0.01	0.01 PA	0.0005	60	0.615	0.615
P2	0.01	0.03 PA	0.0005	60	1.13	0.376
P3	0.01	0.05 PA	0.0005	60	1.63	0.326
A1	0.01	0.01 AA	0.0005	60	0.915	0.915
A1a	0.01	0.01 AA	0.0005	60	0.900	0.900
A2	0.03	0.03 AA	0.0005	60	1.52	0.51
A2a	0.03	0.03 AA	0.0005	60	1.48	0.49
A3	0.05	0.05 AA	0.0005	60	1.88	0.38
A3a	0.05	0.05 AA	0.0005	60	1.86	0.37
A4	0.07	0.07 AA	0.0005	60	2.24	0.32
A4a	0.07	0.07 AA	0.0005	60	2.31	0.33
A1a	0.01	0.01 AA	0.0005	60	0.90	0.90
A10	0.01	0.03 AA	0.0005	60	1.53	0.51
A11	0.01	0.07 AA	0.0005	60	2.35	0.335
A1a	0.01	0.01 AA	0.0005	60	0.90	0.90
A7	0.01	0.01 AA	0.001	60	1.61	1.61
A8	0.01	0.01 AA	0.0015	60	2.5	2.5
A9	0.01	0.01 AA	0.002	60	3.42	3.42
A12	0.01	0.01 AA	0.0005 + 0.0001 BzOH	60	0.67	0.67
A18	0.01	0.01 AA	0.0005	65	1.04	1.04
A19	0.05	0.05 AA	0.0005	65	2.20	0.44
T1	0.01	0.01 TA	0.0005	60	0.98	0.98
T2	0.01	0.03 TA	0.0005	60	2.20	0.73
T3	0.01	0.05 TA	0.0005	60	2.52	0.50
T4	0.01	0.07 TA	0.0005	60	2.68	0.38
B1	0.01	0.01 BA	0.0005	60	1.30	1.30
B5	0.03	0.03 BA	0.0005	60	1.84	0.60
B6	0.05	0.05 BA	0.0005	60	3.23	0.64
B7	0.07	0.07 BA	0.0005	60	3.95	0.56
B1	0.01	0.01 BA	0.0005	60	1.30	1.30
B2	0.01	0.03 BA	0.0005	60	1.87	0.62
B3	0.01	0.05 BA	0.0005	60	3.22	0.65

TABLE I (*continued*)

Run No.	NBC mole 1^{-1}	Aldehyde moie 1^{-1}	Peperidine mole 1^{-1}	T°C	10^6k_1	10^4k_2
B4	0.01	0.07 BA	0.0005	60	4.10	0.58
B1	0.01	0.01 BA	0.0005	60	1.30	1.30
B8	0.01	0.01 BA	0.001	60	2.56	2.56
B9	0.01	0.01 BA	0.0015	60	3.74	3.74
B10	0.01	0.01 BA	0.002	60	5.07	5.07
B11	0.01	0.01 BA	0.0005 + 0.0001 BzOH	60	0.96	0.96
PC1	0.01	0.01 pCA	0.0005	60	6.75	6.75
PC2	0.01	0.03 pCA	0.0005	60	18.0	6.0
PC3	0.01	0.05 pCA	0.0005	60	21.2	4.25
PC4	0.01	0.07 pCA	0.0005	60	25.0	3.57
OC1	0.01	0.01 oCA	0.0005	60	20.5	20.5
OC2	0.01	0.03 oCA	0.0005	60	29.8	13.3
OC3	0.01	0.05 oCA	0.0005	60	37.1	7.4
NA1	0.01	0.01 pNA	0.0005	60	97.0	97.0
NA7	0.01	0.01 pNA	0.0005	60	97.1	97.1
NA2	0.03	0.03 pNA	0.0005	60	125.0	41.5
NA5	0.04	0.04 pNA	0.0005	60	148.0	37.0
NA3	0.05	0.05 pNA	0.0005	60	203	40.5
NA1	0.01	0.01 pNA	0.0005	60	97.0	97.0
NA9	0.01	0.03 pNA	0.0005	60	140.0	46.7
NA8	0.01	0.05 pNA	0.0005	60	212.0	42.5
NA1	0.01	0.01 pNA	0.0005	60	97.0	97.0
NA10	0.01	0.01 pNA	0.001	60	182.0	182.0
NA11	0.01	0.01 pNA	0.002	60	392.0	392.0
NA12	0.01	0.01 pNA	0.0005 + 0.0001 BzOH	60	57.0	57.0
NA15	0.01	0.01 pNA	0.0005 + 0.0001 BzOH	65	115.0	115.0

DISCUSSION

The results in Table I show very clearly the dependence of the reaction rates on the catalyst concentration. In every case studied, a full first order dependence on the piperidine concentration was observed, at catalyst concentrations between 0.0005 and 0.002 mole 1^{-1}. Moreover, plotting rates against catalyst concentration, the curves with the three aldehydes studied in detail, *i.e.*, anisaldehyde, benzaldehyde and *p*-nitrobenzaldehyde, converged at zero, although the absolute magnitude of the rates differed very widely .The conclusion can therefore be safely drawn that there is no significant ionisation of *p*-nitrobenzyl cyanide in ethanol, that the ionisation is directly proportional to the piperidine concentration and that no reaction takes place between the undissociated *p*-nitrobenzyl cyanide molecule and the aldehydes.

Plotting the values of $k/k_{0.001}$ where $k_{0.001}$ is the value of the rate coefficient of the reaction of 0.01 M of aldehyde with 0.01 M of *p*-nitrobenzyl cyanide in the presence of 0.001 M of piperidine and k is the value of the rate coefficient of the same reaction with differing amounts of catalyst, all the points obtained fell very nearly on a straight line, passing through the origin, indicating first order dependence. In Figure 1, the values from the experiments in the presence of 0.005 M of piperidine and 0.0001 M of benzoic acid were plotted at the place corresponding to 0.0004 M of piperidine, and these points too fit the line well.

With each of the above mentioned three aldehydes, experiments were made in which 0.0001 M of benzoic acid was added, to a mixture containing 0.01 M of each of the reactants and 0.0005 M of piperidine. In all three cases the rates fell very sharply, to about 60% of the rate in similar conditions without the acid. This fact further strengthens our belief[1], that only the carbanion formed from the active methylene compound is able to react with the carbonyl group of the aldehydes, that any species in the reaction mixture which represses the ionisation of this methylene group lowers the reaction rates, and that salts of amines cannot be stronger catalysts than the amines themselves[2]. These salts were claimed to act as strong catalysts, owing to an acid-base catalysis scheme proposed by several investigators[3]. We believe that these observations must have a different explanation, possibly a very strong salt effect in solvents of low dielectric constant, which may outweigh the slowing down of the reaction caused by the addition of a proton donor to the reaction mixture. The observed overall rates of the reaction, as can be seen from Table I, are intermediate between first and second order. In the reaction sequence:

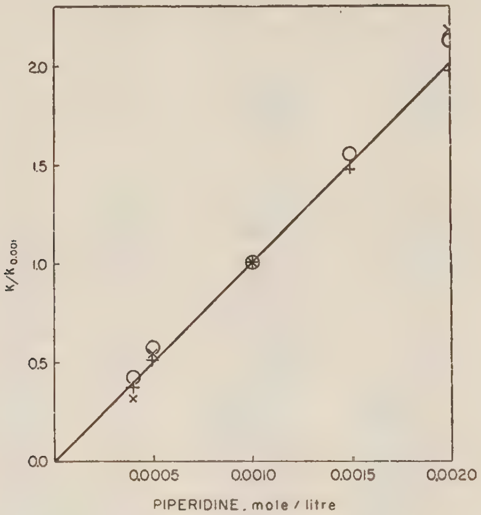
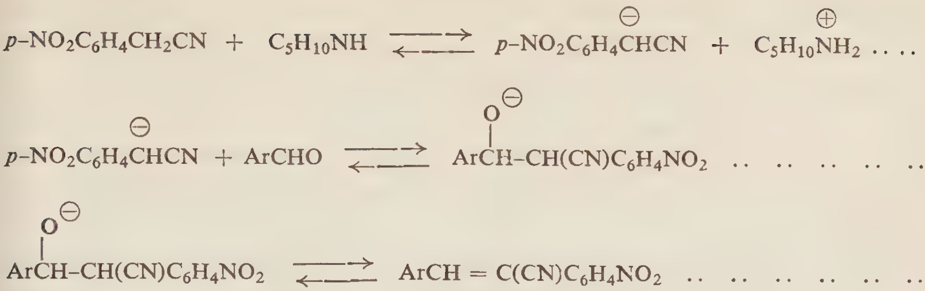


Figure 1
Relative magnitude of the rate coefficients of the reaction of 0.01 M of aldehyde with 0.01 M of *p*-nitrobenzyl cyanide, in the presence of various concentrations of piperidine.

O — experiments with anisaldehyde
+ — experiments with benzaldehyde
× — experiments with *p*-nitrobenzaldehyde



$$p\text{-}NO_2C_6H_4CH_2CN + C_5H_{10}NH \rightleftharpoons p\text{-}NO_2C_6H_4\overset{\ominus}{C}HCN + C_5H_{10}\overset{\oplus}{N}H_2 \ldots\ldots (1)$$

$$p\text{-}NO_2C_6H_4\overset{\ominus}{C}HCN + ArCHO \rightleftharpoons Ar\overset{O^{\ominus}}{\overset{|}{C}}H\text{-}CH(CN)C_6H_4NO_2 \;\; .. \;\; .. \;\; .. \;\; .. \;\; .. \;\; (2)$$

$$Ar\overset{O^{\ominus}}{\overset{|}{C}}H\text{-}CH(CN)C_6H_4NO_2 \rightleftharpoons ArCH = C(CN)C_6H_4NO_2 \;\; .. \;\; .. \;\; .. \;\; .. \;\; .. \;\; .. \;\; (3)$$

we would obtain first order dependence on the catalyst and first order dependence on the active methylene compound, if step (1) were rate determining. Second order overall rates would have to be observed with an additional first order dependence on the catalyst, if step (1) would be fast and step (2) slow. The observed intermediate order is probably the result of the fact that both step (1) and step (2) are rather slow and of comparable order of magnitude. In any case, the first order dependence on the catalyst concentration is reasonable, whatever the actual reaction order in the two reactants may be.

EXPERIMENTAL

The ethanol used as solvent was carefully purified before use. Piperidine, benzoic acid and the aromatic aldehydes were recrystallised or redistilled before use. *p*-Nitrobenzyl cyanide was prepared according to the literature[4].

The reaction products were prepared as follows: 0.01 moles each of the aldehyde and of *p*-nitrobenzyl cyanide were refluxed with 0.1 ml of piperidine in 100 ml of ethanol for six hours. After cooling, the products precipitated, giving yields of 70–75%.

1-(*p*-Nitrophenyl)-1-cyano-2-phenylethylene, m. p.86°[5], 1-(*p*-nitrophenyl)-1-cyano-2-(*p*-methoxyphenyl)-ethylene, m.p. 165°[6], 1-(*p*-nitrophenyl)-1-cyano-2-(*p*-chlorophenyl)-ethylene, m.p. 186°[7] and 1,2-di-(*p*-nitrophenyl)-1-cyanoethylene, m.p. 214°[8], are known compounds. The following new compounds were prepared:

1-(p-Nitrophenyl)-1-cyano-2-(m-methoxyphenyl)-ethylene, m.p. 195° (from ethanol).
Anal. Calcd. for $C_{16}H_{12}O_3N_2$: C, 65.5, H, 4.3%
Found: C, 68.4, H, 3.8%.

1-(p-Nitrophenyl)-1-cyano-2-(4-piperonyl)-ethylene, m.p. 191° (from ethanol).
Anal. Calcd. for $C_{16}H_{10}O_4N_2$: C, 65.4, H, 3.4%
Found: C, 65.2, H, 3.4%.

1-(p-Nitrophenyl)-1-cyano-2-(p-tolyl)-ethylene, m.p. 146–7° (from ethanol or petroleum ether).
Anal. Calcd. for $C_{16}H_{12}O_2N_2$: C, 72.8, H, 4.5, N, 10.6%
Found: C, 72.3, H, 4.7, N, 10.9%.

1-(*p-Nitrophenyl*)-1-*cyano*-2-(*o-chlorophenyl*)-*ethylene*, m.p. 167° (from ethanol or CCl_4).

Anal. Calcd. for $C_{15}H_9O_2N_2Cl$: C, 63.6, H, 3.2 %
Found: C, 63.6, H, 3.6%.

Spectra: Yellow solutions of *p*-nitrobenzyl cyanide in ethanol (λ_{max} 263 mμ, $\varepsilon = 10{,}000$) turned red on addition of piperidine, probably owing to the formation of the carbanion. In the presence of a large excess (2N) of sodium ethoxide the carbanion of *p*-nitrobenzyl cyanide gave the following light absorption in $10^{-4} - 10^{-5}$ molar solutions: λ_{max} 256 mμ ($\varepsilon = 5000$) and λ_{max} 530 mμ ($\varepsilon = 26400$)*.

For use in the kinetic runs, the following data were determined for the reaction products, in 0.02 molar solutions of hydrochloric acid in ethanol as the solvent:

TABLE II

Spectral data for the products $O_2NC_6H_4C(CN) = CHAr$ *in* 0.002 *M methanolic HCl*

Ar —	λ_{max}, mμ	ε_{max}
Piperonyl-	382	37,000
p-Methoxyphenyl-	370	26,500
p-Tolyl-	348	18,200
Phenyl-	334	26,500
p-Chlorophenyl-	338	28,800
o-Chlorophenyl-	324	27,000
p-Nitrophenyl-	336	30,000

At the wavelengths given in Table II, neither the corresponding aromatic aldehydes, nor the *p*-nitrobenzyl cyanide interfered in the measurements.

Kinetic runs. From the reaction mixture, 1 ml samples were taken at intervals of 1 to 10 minutes, depending on the velocity of the reaction. These samples were diluted 25–100 fold with a 0.02 molar solution of hydrochloric acid in ethanol. This procedure stopped the reaction immediately and completely. The percentage reaction was calculated from the amount of the product present in the solution, as measured at the appropriate wavelength. Rate coefficients were calculated from the integrated kinetic equations for first and second order reactions.

NOTE: * We are indebted to Prof. A. Bruylants for a personal communication, according to which the data published in *Helv. Chim. Acta*, **35**, 1131 (1952) for this compound are erroneous. New data communicated to us by Prof. Bruylants are as follows: *p*-nitrobenzyl cyanide in ethanol: λ_{max} 262mμ, $\varepsilon = 9532$; in 1N EtONa: λ_{max} 265 mμ, $\varepsilon = 4200$, and λ_{max} 528 mμ, $\varepsilon = 28800$.

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SOME STEREOCHEMICAL PROBLEMS IN THE ASCORBIN SERIES

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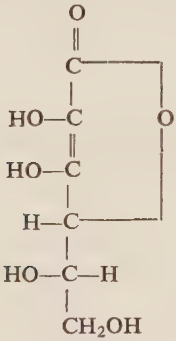
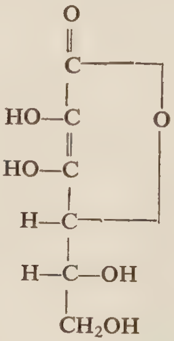
The natural vitamin C, L-ascorbic acid (the enolic form of 2-keto-L-gulono-γ-lactone, I) gives a strong acid reaction in aqueous solutions and is dextrorotatory. Its synthetical stereoisomer, D-arabo-ascorbic acid (isoascorbic acid, II) which differs from the natural vitamin in the configuration of C–5, has the same acidity, but is levorotatory.



(I)



(II)

The rotatory power of both compounds is a function of the *p*H owing to the shift of the equilibrium between the acidic and lactonic states and the enolic and ketonic forms at different grades of acidity or alkalinity.

Compound (II) does not obey in its optical rotation Hudson's lactone rule[1,2] which has been confirmed for numerous lactones in the sugar series.

It was found that the specific rotations of (I) and (II) become identical for a broad range of *p*H, beginning approximately at *p*H 6 up to *p*H 10. Within these bounds the optical rotation is almost constant.

This phenomenon has been confirmed for four different wave-lengths (red, $\lambda = 6200$ Å, yellow $\lambda = 5890$ Å, green $\lambda = 5500$ Å, blue $\lambda = 4360$ Å) and cannot therefore be explained away as an accidental coincidence. The changes of the optical rotation values of (I) and (II) are reversible and the original values are regained on re-establishing the original *p*H.

The ultraviolet absorption spectrum of (I) has been described as dependent upon the *p*H[3,4]. We could not detect any difference between the maxima of the ultraviolet spectra of (I) and (II) at different *p*H.

Conversion of (I) and (II) into dehydro-ascorbic acid (III) and dehydro-isoascorbic acid (IV) respectively, by dehydrogenation with iodine abolishes the convergence of the two *p*H-optical activity curves at *p*H 6–10. The rotatory powers of (III) and (IV) show a strong and very complicated dependence on the *p*H, but their curves remain strictly different.

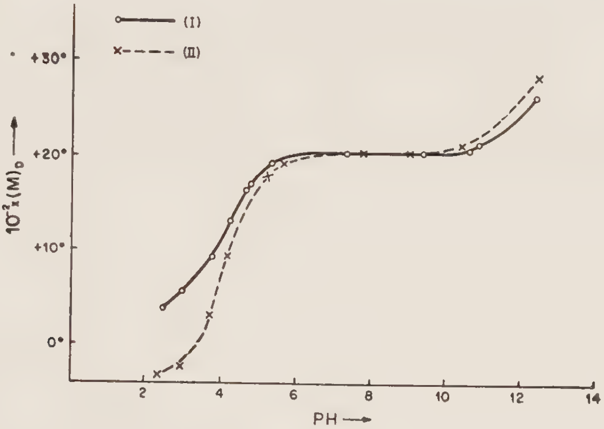


Figure 1
Molecular rotations of L-ascorbic acid (I) and D-arabo-ascorbic acid (II) at different *p*H.

The optical behaviour of 3-methyl ascorbic acid (V), and 3-methyl isoascorbic acid (VI) and also of 2,3-dimethyl ascorbic acid (VII) and 2,3-dimethyl isoascorbic acid (VIII), at different *p*H's was also investigated. In both pairs of these stereoisomerical substances the $[\alpha]_D$-rotation curves remain strictly different for the two components.

It seems therefore that the presence of the dienolic group is essential for the above-mentioned phenomenon.

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LETTER TO THE EDITOR

Evaporation rate of water from open surfaces coloured white, M. R. Bloch and T. Weiss, *Dead Sea Works, Ltd.*

During the night of August 24, 1943 the water of the Dead Sea turned milky white. Chemical analysis proved the colour to be due to carbonate of lime which had suddenly been dispersed throughout the surface brine of the Dead Sea.

The sea level at the end of autumn 1943 was rather high.

Two months later (October), the temperature of the water at a depth of 15 m below the sea level was found to be abnormally low. It was 8°C less than the last record made three years earlier (October 1940).

Both these latter phenomena may be attributed to the whiteness of the Dead Sea brine which reflected the sun's rays, causing a lower temperature and a reduced rate of evaporation.

This hypothesis was proved by a series of experiments carried out in Jerusalem during 1956. White spherical polythene balls of two different sizes (4.5 mm and 2.3 mm diameter) were used to cover surfaces of water in order to imitate the effect of a suspension of white lime particles during evaporation from an exposed surface. White enamelled pots (25 cm high and 23.3 cm diameter) were used as test vessels (Figure 1). In order to minimize any wall effect, good insulation was provided around the walls and under the bottom of the vessels.

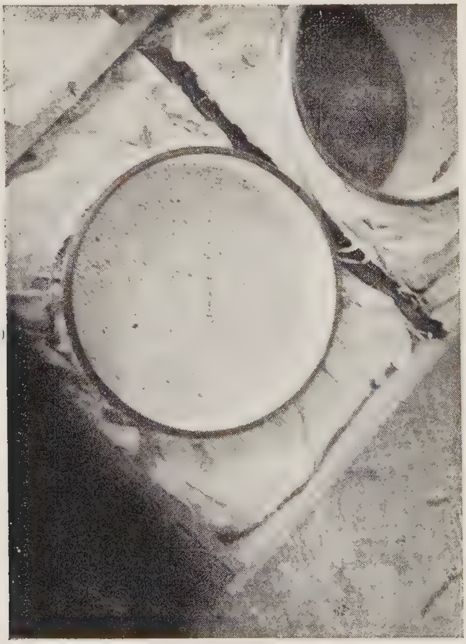

Figure 1

Evaporation from pails with plastic balls (17.X.—17.XI. 1956

The specific gravity of the polythene balls was 0.92. If we consider that the balls were wet, the percentage of submergence must have been about 90 percent. In other words, the exposed part of the balls represented not more than 1/8 of their surface area. The surface of the water exposed between the balls absorbed the infrared radiation. The infrared of the solar radiation constituted about 50 percent of its total.

Experiments made between 17.10.1956 and 17.11.1956 demonstrated that the white balls floating in a water surface reduced the rate of evaporation by approximately 40 percent. It can be expected that the visible part of the solar radiation, which would normally be absorbed in vessels with a dark floor, is reflected by the white balls. Only the infrared part is absorbed and used for evaporation.

As a check against the possibility that the balls reduced the rate of evaporation through the reduction of the surface area of the water and not by their colour, a similar experiment was made with black balls. No appreciable alteration of the rate of evaporation could be noticed in comparison with water without any balls. In Figure 2 the experiments are represented by three graphs: for water, for water with white balls and for water with black balls.

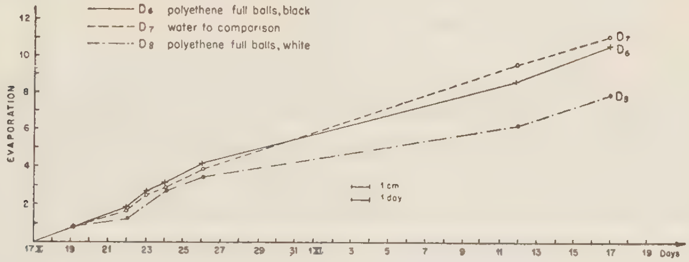

Figure 2
Vessels of the experiment: pails a 23.8 cm
h 25.0 cm
isolation: bricks, paper, rag

Thus the influence of the white colour of the balls was proved. Although neither the reflectivity of the carbonate of lime (as found in the Dead Sea) nor that of the white balls has yet been established by the experiment, it can be assumed that their reflectivities are very similar.

It is assumed that white balls of polythene or a similar material, slightly lighter than water, might be useful for the prevention of water losses from open large scale reservoirs. The balls might have a tendency to respread over the whole free surface of such a reservoir after disturbances. They are also easily separated from the water when water is taken for use.

The authors are indebted to M. van Mentz, I. Schnerb and H. Tabor for helpful discussion and to L. Robitschek for technical cooperation.

We wish to thank the Ford Foundation for assistance and the Dead Sea Works Ltd. for permission to publish the paper.

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* At the time this paper goes to press, the Dead Sea had turned white again (end of August 1959). The phenomenon is under observation.

PAPERS PRESENTED AT THE XXVth MEETING OF THE ISRAEL CHEMICAL SOCIETY

(These abstracts were submitted after closing date for printing of Proceedings published in the Bulletin of the Research Council of Israel, Section A — Chemistry, Vol. 8, No. 3)

Photochemical reactions in crystals of organic nitrocompounds

G. M. J. Schmidt and Ph. Coppens, *Department of X-Ray Crystallography· The Weizmann Institute of Science, Rehovoth*

p-Nitrophenol crystallises in two modifications. The α form turns red when irradiated by sunlight, the β form and solutions of *p*-nitrophenol being light-stable.

Both crystal structures have been solved. Differences between the two structures which may allow for the different photochemical behaviour will be discussed.

The first step of the reaction is thought to be an attack of the nitrogroup on the aromatic nucleus of a second molecule, in analogy with the intramolecular photochemical reaction shown by several ortho-substituted aromatic nitrocompounds.

The charge distribution in the first excited state of the *p*-nitrophenol molecule supports this view.

Dimerisation in the solid state of cinnamic acid and some of its derivatives under the influence of sunlight

M. D. Cohen, M. Rim, G. M. J. Schmidt and F. Sonntag, *Department of X-Ray Crystallography, The Weizmann Institute of Science, Rehovoth*

On exposure to sunlight, different crystalline modifications of cinnamic acid undergo dimerisation in the solid state. Diphenyl-cyclobutane-dicarboxylic acids are formed by the reaction between the nonaromatic double-bonded carbon atoms of the monomer.

Some of the nucleus-substituted cinnamic acids have been investigated and found to behave in an analogous way.

The occurrence of the reaction and the type of dimer formed depend on the arrangement of the monomer in the crystal lattice.

Different polymorphic modifications of the same compound are shown to react differently, and in some cases light-stable crystalline modifications have been found.

BOOK REVIEWS

MECHANISM AND STRUCTURE IN ORGANIC CHEMISTRY, by Edwin S. Gould, pp. X + 790, Henry Holt and Co., 1959, New York, $12.50

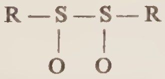
This textbook of physical organic chemistry is mainly intended for the use of graduate students working for a higher degree. It covers the main subjects of this field, such as the theory of the structure of molecules, acids and bases and the most important reaction types. The main distinction of this book lies in the inclusion of a large number of exercises at the end of each chapter. Some of these exercises are rather difficult, and (as the answers are not given) will surely cause unpleasant moments for unfortunate instructors working with unihibited students (e.g. (p. 763) "predict the major product resulting from the reaction

$$Ph_2Se_2 + (i\text{-Bu})_2CHOH + HgCl_2 \xrightarrow{160^\circ} \text{''}$$

or (p. 512) "Explain that ...... the mass-law effect is much more commonly observed in SN1 reactions, than in E1 reactions".

An interesting feature of the book lies in the attempt to give a systematic summary of the methods used for determining reaction mechanisms (p. 127–194). The readers attention is drawn to the imitations of the methods used, and to the ambiguities which may arise in the interpretation of experimental data.

On the whole, this is a readable and well-balanced textbook, even though the author includes discussion of some topics which in this reviewers opinion are at present too controversial and will tend to confuse students rather than further their understanding (e.g., p. 300, p. 388 etc.). Similarly, what is permissable in a research paper should not appear in a textbook: Professor Gould's personal preference for writing semipolar double bonds in the form of a single bond, undistinguished from ordinary C-H or C-X bonds. results throughout the book in structural formulae where oxygen atoms are apparently univalent, sulphur and selenium atoms apparently tervalent, etc. Thus, formulae of the type



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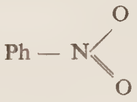

are consfuing not only to the reader, but even to the author himself, who several times "relapses" into the use of the generally accepted forms (pp. 205, 213, 433, etc.).

Saul Patai

AROMATIC SUBSTITUTION: NITRATION AND HALOGENATION, by P. B. D. de la Mare and J. H. Ridd, 1959, vii + 252 pages, Butterworths Scientific Publications, London, 50 s.

After introductory chapters on the qualitative electronic theory of organic chemistry, and on methods of investigation of reaction mechanisms, the book deals with the various aspects of electrophilic aromatic nitration including preparative methods, kinetic studies and mechanisms, structural and substituent effects as well as nitrosation and nitrating agents. This is followed by a similar treatment of halogenation (chlorination, bromination and iodination). Electrophilic displacement of groups other than hydrogen in nitration and halogenation and rearrangements involving these substitutions are also discussed. The book deals not only with aromatic substitution in benzene, biphenyl, or polycyclic aromatic compounds but also in heterocyclic compounds and non-benzenoid hydrocarbons.

The authors have adopted the qualitative electronic theory of organic chemistry as developed especially by Ingold and Hughes in dealing with the subject of aromatic substitution although at the end of the book they give a concise review on modern more quantitative treatment using molecular orbital calculations.

The reviewer feels that it would have been useful to have included in the introductory part a short discussion on the methods used in identifying the various structural isomers formed in substitution reactions.

In general, the book is well written, and the vast experimental and theoretical work that has accumulated in the literature as regards the topic of aromatic substitution has been well summarised, organised and critically presented. The subject matter is covered extensively in its various aspects and a wealth of references up to 1957–58 is given.

Further books on other aspects of aromatic substitution would be appreciated.

Albert Zilkha.

ORGANIC CHEMISTRY, by Donald J. Cram and George S. Hammond, pp. XV + 712. ($8.50, McGraw Hill, New York).

Text-books of organic chemistry are generally based on a division of the subject matter according to classes of compounds. Most authors take jealous care not to mix compounds which belong to different "boxes" *i.e.*, aliphatic alcohols are kept apart from phenols, alkenes from aromatic compounds etc., etc. Even the authors of more modern textbooks, who put more and more emphasis on the structural, mechanistic and theoretical side of organic chemistry cannot liberate themselves from the "boxing" of the subject matter and generally try to fit in the theoretical parts into the general framework of the descriptive content of their books.

Cram and Hammond are ,as far as I am aware, the first authors who organised the material of their textbook according to reactions rather than according to classes of compounds.

The first four chapters of the book (p. 1–86) give a general introduction on structure, nomenclature and main classes of compounds. The next chapters (p. 87–198) deal with the chemical bond, stereochemistry and correlation between structure on the one hand and physical and chemical properties on the other, and with the characterisation of organic reactions. After this come ten chapters (p. 199–478) lon various classes of organic reactions, classified according to their mechanisms.To give an example, the following reactions, which vary widely by the "classical" concepts, appear in the same chapter ("Nucleophilic substitution reactions at saturated carbon"): solvolysis of alkyl halides and reactions with various oxy-anions to give alcohols, ethers or esters, alkylation of phenols, formation of amines, azides and nitrocompounds, cleavage of ethers, reactions of organo-metallic compounds, etc. The last nine chapters (p. 479–678) deal with additional selected topics, such as heterocyclic compounds, various natural products, polymers, etc.

Obviously, the advantages and disadvantages of this teaching method as compared with the classical one, can (and probably will) be discussed endlessly. This book is adapted to the courses given by the authors, and its use will be difficult for students who are expected to learn and take examinations by other methods.

Nevertheless, I believe that the authors' hope, that "our organisation eliminates the waste usually involved in reorientation of students' thinking when they pass from an elementary course either to an advanced course or to research", is a very well based one, and the use of this textbook is to be recommended very warmly.

Saul Patai
Department of Organic Chemistry
The Hebrew University of Jerusalem

The International Union of Pure and Applied Chemistry has decided to publish an official journal PURE AND APPLIED CHEMISTRY.

The journal will appear at irregular intervals as material is available. It will be published in parts; four parts to a volume, each volume containing about 600 pages. The subscription will be approximately £5.5.0 per volume.

The journal will contain the lectures or papers read at symposia organised or sponsored by IUPAC, reports of IUPAC Commissions, Divisions and Committees, and other material which the IUPAC Authorities may decide to include.

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Volume 8A, Number 4, December 1959

BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

Section A
CHEMISTRY

Bull. Res. Counc. of Israel. A. Chem,

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